51. IWK

Internationales Wissenschaftliches Kolloquium
International Scientific Colloquium

PROCEEDINGS 11-15 September 2006

FACULTY OF ELECTRICAL ENGINEERING AND INFORMATION SCIENCE

INFORMATION TECHNOLOGY AND ELECTRICAL ENGINEERING - DEVICES AND SYSTEMS, MATERIALS AND TECHNOLOGIES FOR THE FUTURE

Startseite / Index:
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TECHNISCHE UNIVERSITÄT
ILMENAU

Impressum

Herausgeber: Der Rektor der Technischen Universität Ilmenau
Univ.-Prof. Dr. rer. nat. habil. Peter Scharff

Redaktion: Referat Marketing und Studentische Angelegenheiten
Andrea Schneider

Fakultät für Elektrotechnik und Informationstechnik
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Redaktionsschluss: 07. Juli 2006

Technische Realisierung (CD-Rom-Ausgabe):
Institut für Medientechnik an der TU Ilmenau
Dipl.-Ing. Christian Weigel
Dipl.-Ing. Marco Albrecht
Dipl.-Ing. Helge Drumm

Technische Realisierung (Online-Ausgabe):
Universitätsbibliothek Ilmenau
ilmedia
Postfach 10 05 65
98684 Ilmenau

Verlag:
Verlag ISLE, Betriebsstätte des ISLE e.V.
Werner-von-Siemens-Str. 16
98693 Ilrnenau

ISBN (Druckausgabe): 3-938843-15-2
ISBN (CD-Rom-Ausgabe): 3-938843-16-0

Startseite / Index:
http://www.db-thueringen.de/servlets/DocumentServlet?id=12391

51st Internationales Wissenschaftliches Kolloquium
Technische Universität Ilmenau
September 11 – 15, 2006

I. Krastev

Self-organized periodic structures in silver alloy electrodeposits

Silver is a noble metal with excellent properties like the best electrical conductivity among the metals, best thermal conductivity, best reflectance of the visible light, some bactericidal properties, chemical resistance etc. To correct some disadvantages of the metal, such as its low hardness and wear resistance, as well as the tarnishing in the atmosphere with even small amount of sulphur, silver is alloyed with small amounts of other metals like antimony, bismuth, indium, tin, lead, cadmium etc. The mechanical properties of the electrodeposited alloys are enhanced in the case small amounts of the alloying element are co-deposited and solid solution of this element with silver is formed. There is always some compromise between the enhancement of the mechanical properties of silver and the worsening of its electrical or thermal conductivity. In most cases the silver lattice is expanded due to the co-deposited metal atoms incorporated therein and this causes an increase in the micro-hardness, abrasion resistance and internal stress of the deposits depending on the amount of the alloying element in the coating. Otherwise the composition of the electrodeposited alloy can be influenced by the electrolysis conditions, like metal ion concentrations in the electrolyte, temperature, current density, agitation and especially by different complex forming agents for both metals. So, under appropriate conditions, for example at high current densities or deposition potentials, i.e. carrying the electrodeposition under conditions far from equilibrium, it becomes possible to co-deposit larger amounts of the alloying element than needed for the saturation of the silver lattice. This leads to spontaneous formation of other phases on silver basis richer of the alloying element. The simultaneous appearance of two or more phases in the electrodeposited alloy arise the question about their distribution in the coating as well as on its surface. Having in mind that the electrolytic cell is an open system where materials and energy can be exchanged with the surroundings, we can conclude that at strong deviation from the equilibrium state, like deposition under limiting current density at least for the more noble metal, for systems of regular type according to Brenner [1], it is possible to observe self-organisation phenomena and formation of ordered structures with broken symmetry not only in space, but also both in space and time. Such structures were observed for the

first time about 60 years ago in 1938 by E. Raub and A. Schall [2] in Germany during electrodeposition of silver-indium alloys (Figure 1).

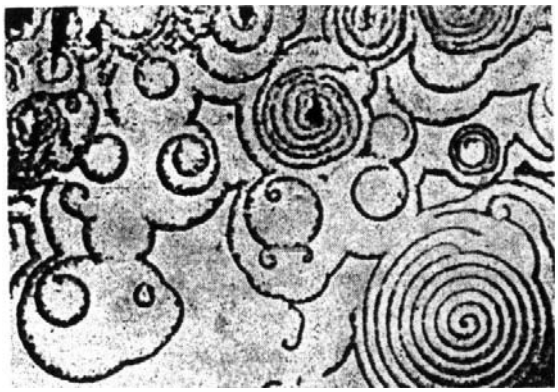

Fig.1. Spiral structures in electrodeposited Ag-In alloy observed by E. Raub et.al. [2].

About 50 years later similar structures were observed during electrodeposition of silver-antimony alloys [3]. On the surface of the electrode, the formation of dynamical periodic structures, such as straight waves (Fig. 2), spiral structures with different topological charge (number of arms up to 5 and more) (Fig. 3) and target patterns (Fig. 4) is observed.

Fig.2. Straight waves

Fig.3. Spiral structures with different topological charges

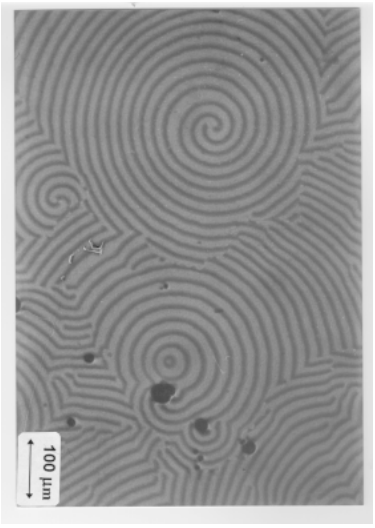

Fig.4. Two armed spiral and target pattern

The upward movement of the waves suggest the decision, that the natural convection in the electrolyte plays an important role in the formation of the structures. This hypothesis was confirmed by electrodeposition of the alloy, under conditions leading to the periodic structures, in a strong magnetic field (5T) [4]. The magnetohydrodynamic force induced an electrolyte motion in horizontal direction which suppressed the upwards motion of the electrolyte due to the natural convection. Under such conditions the movement of the waves in the horizontal direction, i.e. in the direction of the hydrodynamic flow was observed and the waves were oriented perpendicular to the direction of electrolyte motion. The autocatalytic step needed for the structure formation have been shown to be the deposition of antimony on its own substrate, with a potential depolarization of about 200 mV compared to the deposition on silver substrate [4]. By in situ measurements during electrodeposition it was possible to determine the rotation velocity of the spiral

structures, which was about 8 deg.s^{-1} [5]. The upwards movement of waves with different antimony content leads to spontaneous formation of layered electrodeposits with layers of different antimony content and therefore possible with different phase composition (α-, ζ-, ε- and pure Sb-phases are observed) and properties. The properties of the electrodeposited coatings with different antimony content, as well with spatio-temporal structures on the electrode surface were investigated systematically, showing the changes in their internal stress, hardness, abrasion resistance, roughness, electrical contact resistance and plug-in forces depending on the antimony content in the monolayer [6], as well in the cyclic modulated multilayer Ag-Sb coatings [7].

The formation of spatio-temporal structures was also observed during electrodeposition of Ag-Bi-alloys [8], [9]. Using different amounts of some complex forming agents, for example KSCN or KCN for silver, it is possible to change its deposition potential in such a way, that the deposition starts at more negative potential and the dissolution at more positive potential than the respective reactions of bismuth, which allows the deposition of Ag-Bi alloys with any desired percentage [8]. The phase composition of the alloys electrodeposited at high current densities or potentials comprises fewer phases than the Ag-Sb alloy and consists only of a solid solution of bismuth in silver and a pure bismuth phases [9]. The coatings are very heterogeneous and in the cross-section as well as on the surface of the electrode the separate regions of the different phases are clear visible. At bismuth contents between 40 and 60 wt. % the self-organization of both phases in quasi-periodic structures can be observed on the electrode surface [9] (Figures 5 and 6).

The Ag-Bi alloy coatings are matt and grey. They have compressive internal stress and lower hardness and abrasion resistance than pure silver and silver-antimony alloy coatings, but very good antifriction properties [9]. It was shown that the electrodeposition of bismuth on silver substrate leads to formation of island layers, which does not allow the deposition of well defined continuous cyclic modulated multilayer alloy coatings [10,11].

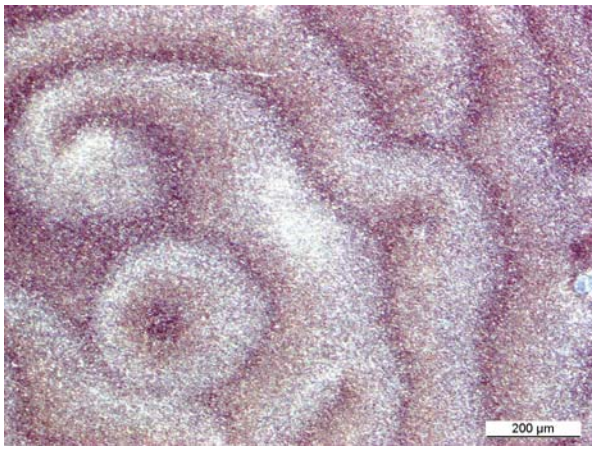

Fig.5. Spirals and target patterns on the surface of an Ag-Bi coating

Fig.6. Surface of an Ag-Bi alloy coating Height of the image 1 cm.

Silver is also alloyed with indium in order to reduce its tarnishing and to produce coatings with good antifriction properties. Using silver electrolytes on cyanide basis one has to solve the problem with the precipitation of the insoluble indium hydroxide in the alkaline solutions. For this purpose a special procedure was developed [12,13]. Nuclear magnetic resonance measurements show the possibility of complex formation between indium ions, cyanide ions and Glucose, the last often used in similar electrolytes. In this complicated complex, the degradation products of the Glucose in the alkaline medium are the closest to the indium ion situated ligands [14]. In this electrolyte at different metal concentration ratios and appropriate current densities the formation of beautiful spatio-temporal structures can be observed [15,14] (Figure 7).

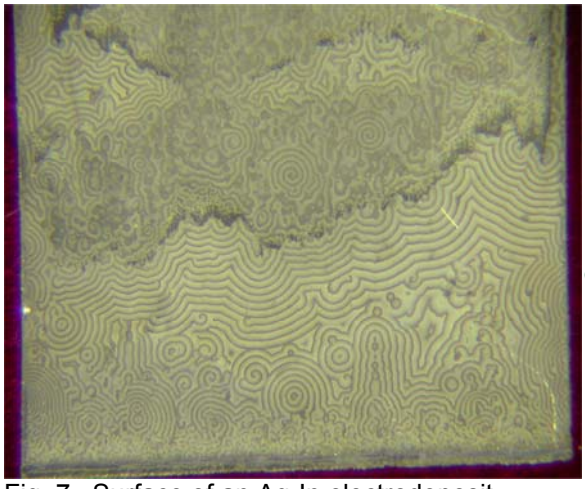

Fig. 7. Surface of an Ag-In electrodeposit Width of the image 1 cm

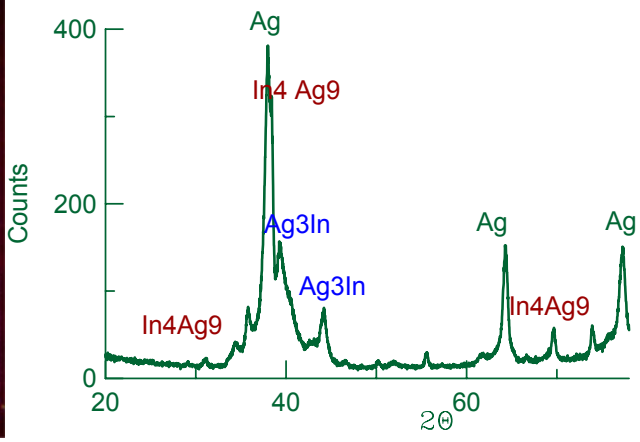

Fig. 8. X-ray diffractogramm of Ag-In electrodeposit with spatio-temporal structures

Almost straight waves, spirals and target patterns are observed side by side on the electrode surface. The x-ray analysis show in the case of self-organized structure

formation the simultaneous presence of three phases in the electrodeposited coating – a solid solution of indium in silver, and the phases Ag_3In and In_4Ag_9 (Figure 8). We suggest that the light areas of the formed structures contain the solid solution of indium in silver, but which one of the other phases forms the dark parts of the structures remains still not clear.

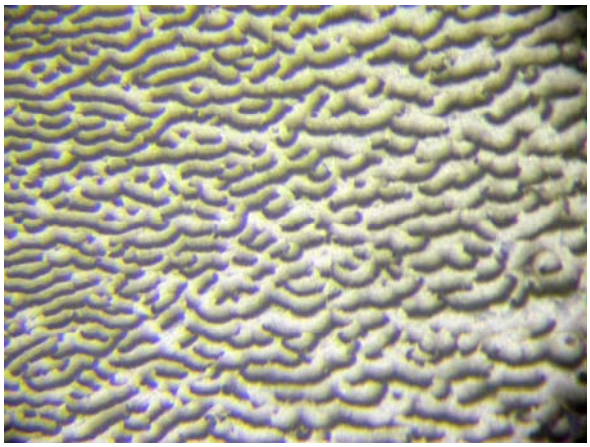

Fig. 9. Surface of an Ag-Sn alloy coating

The self-organized formation of spatio-temporal structures is a phenomenon which needs to be discovered in electrodeposited coatings of many other alloys. Recent investigations show the formation of similar structures during electrodeposition of silver-tin alloys [15] (Fig. 9), where the experiments are still in progress.

Acknowledgements: The author is thankful to Deutsche Forschungsgemeinschaft (DFG) for the support of Project 436 BUL 113/ 97-2 and to all his co-authors of the cited publications.

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